

PACS numbers: 68.37.Lp, 68.55.Jk, 73.61.At

STRUCTURE AND ELECTROCONDUCTIVITY OF THE NANOCRYSTALLINE CoNi THIN FILM ALLOYS

V.B. Loboda, V.O. Kravchenko, Yu.O. Shkurdoda

Sumy State Pedagogical University,
87, Romenska Str., 40002, Sumy, Ukraine
E-mail: vkravchenko@yandex.ru

Structure, phase composition and electroconductivity of nanocrystalline CoNi thin film alloys are investigated. During the I-st cycle of thermal stabilization the grain size increases from approximately 5 nm to 110-200 nm. Films with Co content less than 70 mass % have the single-phase composition with the fcc-lattice. Increase in the lattice parameter, which can be described by the Vegard's rule, is observed with the growth of Co concentration. At Co content more than 75 mass % the annealed films have the two-phase fcc-hcp composition. Quadratic temperature dependence of the resistivity, which is also observed for the single-layer films of pure ferromagnetic metals, is inherent to the films of a given alloy. Using analysis of the size dependences of electroconductivity the concentration dependence of the resistivity is plotted.

Keywords: THIN FERROMAGNETIC FILMS, ALLOY, CRYSTAL STRUCTURE, PHASE COMPOSITION, RESISTIVITY.

(Received 04 December 2009, in final form 16 December 2009)

1. INTRODUCTION

Thin films based on ferromagnetic metals and their alloys are proved to be very promising materials from the point of view of their application in technics (microwave engineering, motion sensors, etc.) and microelectronics. In particular, their application is possible while constructing the magnetic recording media [1-3], magnetic field sensors [4] et al. During last years the interest in these materials is also conditioned by the possibility of formation of multilayer structures (on their basis) with the giant magnetoresistance. We have to note, that a great deal of experimental investigation results of the thin ferromagnetic film properties (structure, phase composition, electroconductivity, magnetoresistance, the Hall effect, etc.) has been accumulated recently. Often investigation concerns the study of the structure and its influence on the magnetic properties, and the sample composition is chosen using the known characteristics for bulk material (invar alloys, permalloys, etc.). Binary CoNi alloy [5], which can be promising, in particular, for the magnetic memory and recording media formation, is one of such materials. Properties of the obtained samples (electroconductivity, coercivity, saturation magnetization and others) can be changed in certain range by varying the element content of alloy and its structure and phase state. The given alloy has ferromagnetic properties over the whole range of element concentrations and unlimited solubility in the solid state with the solid solution formation based on the fcc- or hcp-lattice (except of the small two-phase region).

As the analysis of publications shows, while using the thin-film materials it is necessary to take into account such features, which are inherent to the films themselves. First of all, this concerns the size effects, in particular, the phase one (for example, possibility of changing the phase equilibrium boundaries), the external one (influence of the sample external surfaces) and the internal one (peculiarities of the film structure state and, as a result, change in the kinetic characteristics), that can lead to substantial differences of the film properties in comparison with the bulk samples of the same composition.

Based on the aforesaid, the aim of the present investigation is to study the structure and element concentration influence on the electroconductivity of CoNi thin film alloys.

2. SAMPLE PRODUCTION AND INVESTIGATION TECHNIQUES

Film deposition was realized in the vacuum plant VUP-5M in vacuum of the order of 10^{-3} Pa on the substrates of room temperature. For condensation the substrates of two types were used. Samples for the electroconductivity investigations were deposited on the amorphous non-orienting substrates of the polished optical glass. KBr cleavages, coated by amorphous carbon film to provide the conditions of film formation, which are identical to the main samples, were used as the substrates for the electron-microscopic investigations.

The electron-beam evaporation method was applied to obtain the films. As the initial material the bulk samples of CoNi alloys were utilized. To produce them we used pure (not worse than 99,9%) initial metals (Co and Ni) taken in the required ratio. Samples were melted in high vacuum with holding at the temperature close to the melting one to provide the homogeneity. During the condensation we performed the approximate estimation of the thickness using the resistance of the special sample, which henceforth was also used for the thickness measurements by the interference technique. Thickness of the deposited films was determined by the calculations using the known relation for distribution from the source with a small surface area [6]. In this case we utilized the measured by interferometer MII-4 film thickness deposited opposite the evaporator.

Obtained samples underwent the thermal stabilization treatment during three cycles according to the scheme "heating up to 700 K – keeping at the maximum temperature – cooling in the vacuum of 10^{-3} Pa". Heating rate was 3-5 K/min. During the thermal stabilization temperature was controlled by the differential chromel-alumel thermocouple (the temperature measurement error did not exceed 5 K). Thermal treatment during three cycles allowed to obtain the films with stable properties, in particular, the temperature dependence of the electrical resistance was reproduced in the second, the third and further cycles with high accuracy. Sample resistance was controlled using the digital voltmeter V7-23.

Film resistivity was calculated using the known geometrical sizes of the samples (length a , width b , and thickness d) and resistance R based on the relation $\rho = adb^{-1}R$. Calculation error of the resistivity was defined, first of all, by the thickness measurement error and was 5-10% for the films with thickness more than 50 nm and 10-15% for thinner films.

Based on the experimental data we have plotted the dimension dependences $\rho(d)$, using which it is possible to find the asymptotic values of the resistivity for infinitely thick films and the kinetic coefficients [7].

Investigations of the film structure were performed using the transmission electron microscope EM-125. Samples for the electron microscopy were obtained by the substrate dilution (KBr) in distilled water and by catching of the free film using the microscopic gauze. Both the unannealed and annealed (which underwent the thermal treatment as well as the samples) films were used for investigations.

Study of the phase composition of the samples was carried out using the fast electron diffraction in the device UEMV-100K operated in the electron diffractometer mode. Aluminium film was used as the standard sample while calculating the interplanar spacings and lattice parameters. Determination of the interplanar spacings was performed by the measured (using the comparator IZA-2) diameters of diffraction rings in two mutually perpendicular directions. Then the lines of each phase were selected, the interference indexes of the lines were determined, and the lattice parameters (using quadratic forms for the corresponding syngonies) were calculated.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Structure and phase composition

CoNi alloys in the bulk state have the relatively simple phase diagram. Pure Ni is a monomorphous metal, and in the whole temperature range of existence in the solid state it has the fcc-lattice (structure type A1) with parameter $a = 0,35243$ nm [8]. Co has two polymorphous modifications: the low-temperature α -phase (the hcp-lattice, structure type A3, parameters $a = 0,2507$ nm and $c = 0,40686$ nm) and the high-temperature β -phase, which remains stable to the melting temperature (the fcc-lattice, structure type A1, $a = 0,3548$ nm). The start temperature of the transition α -Co \rightarrow β -Co is 690-700 K, temperature of the reverse transition is 676 K [8].

In accordance with the data [9, 10] CoNi alloys with Co content up to 65-67 mass % at room temperature form the substitutional solid solutions with the fcc-lattice in the whole temperature range of the solid state. For $c_{Co} > 75$ mass % at 300 K solid solution has the hcp-lattice based on α -Co, and with the temperature rise the fcc-lattice based on the β -Co is formed (temperature of the transition hcp \rightarrow fcc depends on the element concentration). In the intermediate concentration region the two-phase composition (fcc + hcp-solid solutions) is observed.

Our investigations of the phase composition showed, that the same behavior is also observed for the film alloys. For the unannealed films with $c_{Co} \leq 70$ mass % the lines of the fcc-phase only are fixed on the electron-diffraction patterns. In this case the diffraction maximums are broad that implies about the small grain size. Sample annealing does not lead to the change in the phase composition of these films. Due to thermal stabilization the lines on the electron-diffraction patterns become narrower and more intensive.

At Co content of 75 mass % films in the initial state, most likely, also have the fcc-lattice. In this case analysis of the electron-diffraction patterns is difficult, since lines are rather broad due to the film dispersity, and the interplanar spacings are almost equal for the most intensive lines of the fcc- and the hcp-lattices. Annealing to the temperature 500-700 K leads to decrease of the line width, and lines of both phases are fixed on the electron-diffraction patterns. In this case the line intensity of the fcc-phase is larger, that can be conditioned both by its larger volume content and the large multiplicity factors for the corresponding planes of the fcc-lattice.

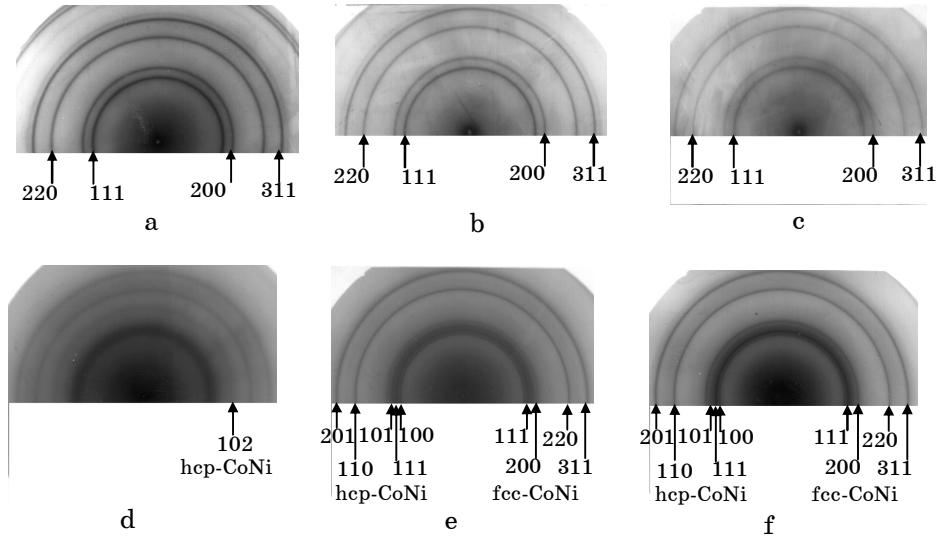


Fig. 1 – Phase composition of the annealed (*a-c, e, f*) and the unannealed (*d*) CoNi films. Co content: 10 mass % (*a*), 30 mass % (*b*), 70 mass % (*c*), 80 mass % (*d, e*), 90 mass % (*f*)

For the unannealed samples with $c_{\text{Co}} \geq 80$ mass % lines of the hcp-lattice are observed in complete accordance with the state diagram. This can be asserted by the presence of the line (102), which is absent for the fcc-lattice.

As a result of the annealing the two-phase composition (fcc + hcp) is observed in these samples, and intensity of the hcp-reflections is significantly larger. Obviously, at the heating up to 700 K the phase transition with the high-temperature fcc-phase formation occurs in the samples. But in spite of the relatively slow cooling the inverse transition does not completely occur, and some amount of the fcc-phase remains in the sample. Possibly, the reason is the phase size effect. According to the data [11] in Co particles of the small size the existence of the fcc-phase is possible at temperatures lower than the termination temperature of the inverse transition. Due to the rather significant spread in grain sizes (as data of the electron-microscopic investigations for our samples indicates) for the part of smaller grains ($L = 50-70$ nm) the fcc-phase can remain stable, while in the large grains the hcp-phase is formed after cooling.

Growth in the concentration of Co atoms leads to increase in the fcc-lattice parameter (see Fig. 2) in almost linear fashion, i.e., the Vegard's rule holds for the given system. Such results (taking into account the error of parameter determination) are presented in [12]. In this paper the broadening of two-phase regions on the phase diagram of film alloys is also noted in comparison with the bulk samples that is observed in our case.

Analysis of the electron-microscopic pictures shows that for the unannealed films the dispersed structure with the grain size less than 5 nm is observed (Fig. 3a), and this explains the substantial width of diffraction maximums. During the thermal stabilization the considerable increase in the grain size is observed. Microstructure analysis performed gives the value of 110-200 nm (Fig. 3b,c,d) for the average grain size.

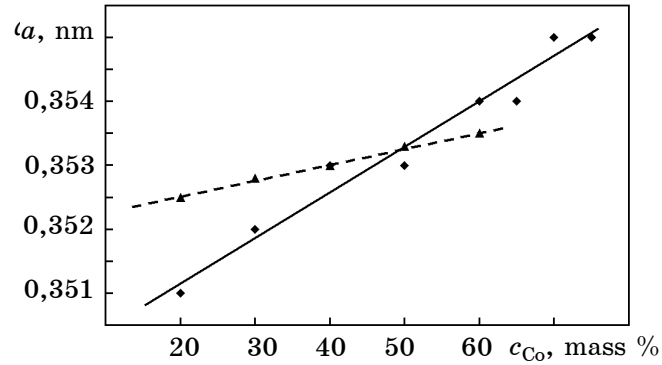


Fig. 2 – Dependence of the fcc-lattice parameter versus the Co concentration for CoNi alloys. \blacklozenge – our data, \blacktriangle – data of Ref. [12]

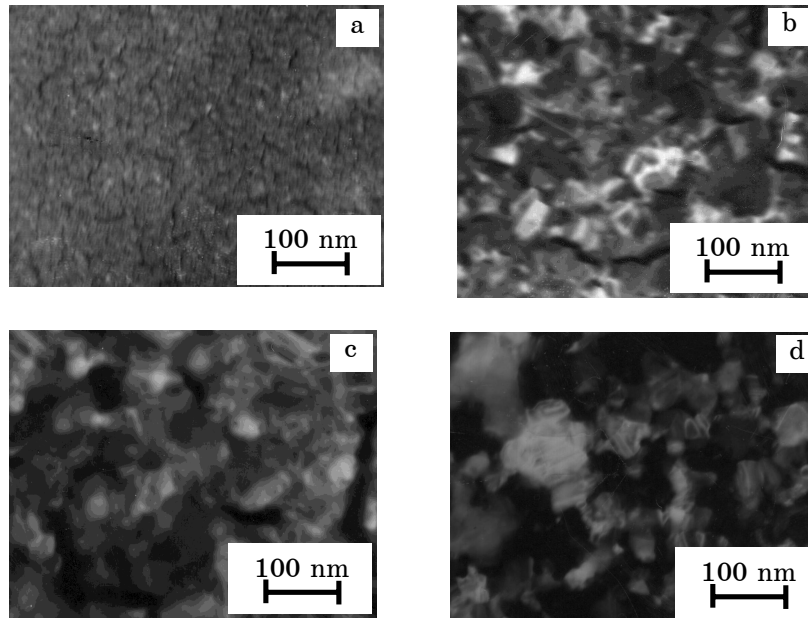


Fig. 3 – Microstructure of CoNi film alloys. Typical structure of the unannealed film: $c_{Co} = 70$ mass % (a), film structure after thermal treatment: $c_{Co} = 10$ mass % (b), $c_{Co} = 50$ mass % (c), $c_{Co} = 90$ mass % (d)

3.2 Resistivity of CoNi thin films

While heating in the first cycle of thermal stabilization the substantial irreversible decrease in the resistance (Fig. 4a) was observed for all samples. Large resistivity values of the films deposited on unheated substrate (which are 2-3 orders more than for the bulk samples) are connected with their structure imperfection and dispersity. Annealing of the samples leads to the recrystallization processes in the film, increase in the grain size, and as a

result to the decrease in the resistivity. Resistivity decreases by 50-100 times for the thinnest films ($d < 30$ nm), while for thicker samples it is reduced by 5-10 times only. During further thermal treatment (2-3 cycles) the polytherms of resistance almost coincide. In this case the temperature dependence of the resistivity is plotted in $\rho-T^2$ coordinates (Fig. 4b) that is typical for the ferromagnetic metals [13] and connected with the electron-magnon interaction.

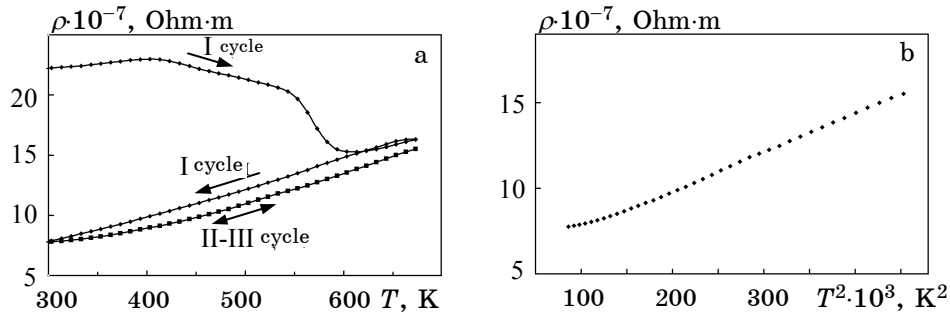


Fig. 4 – Typical temperature dependence of the resistivity during the thermal stabilization (a); the same dependence (2-3 cycles) in directional coordinates (b)

Resistivity of CoNi films is the dimension-dependent quantity, and behavior of the dependence is the same as for the single-layer films of pure metals. With the thickness growth this quantity tends to the asymptotic value, which corresponds to the infinitely thick film (ρ_∞). Based on the determined (from the dependence $\rho(d)$) value of ρ_∞ we have plotted the concentration dependence $\rho(c_{Co})$. As seen from Fig. 5, with modification of the film composition the resistivity changes a little passing through the maximum. The same dependence is obtained in [14] for bulk CoNi alloys. We have to note that values of ρ_∞ for the films substantially exceed the resistivity value of bulk Ni and Co and their alloys ($\rho_0 = (5-7) \cdot 10^{-8}$ Ohm·m).

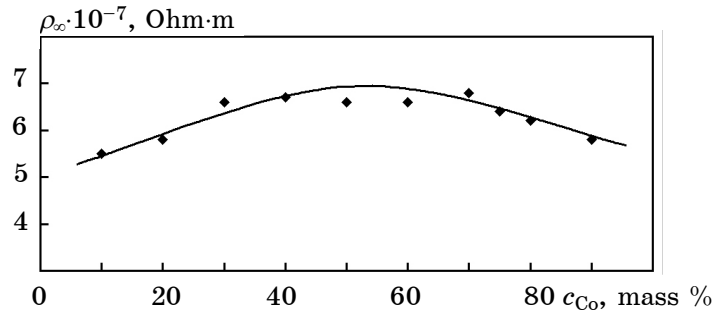


Fig. 5 – Concentration dependence of the resistivity ρ_∞ for films of CoNi alloy

4. CONCLUSIONS

1. In accordance with the electron-microscopic and diffraction investigations CoNi film alloys after condensation have the pronounced dispersed structure with the grain size < 5 nm.

2. Thermal stabilization treatment leads to increase in the average grain size up to 110-200 nm due to the recrystallization processes and is accompanied by the irreversible decrease in the resistivity of the samples during the I-st heating cycle.
3. Films of CoNi alloys with Co concentration less than 70 mass % have the single-phase composition with the fcc-structure, and its lattice parameter increases with Co content. Further growth of Co concentration leads to the two-phase system formation after thermal stabilization (CoNi solid solutions with the hcp- and fcc-lattices).
4. Temperature dependence of the resistivity of the investigated film alloys is characterized by the quadratic dependence, which is typical for the ferromagnetic metals.
5. Dependence of the asymptotic value of the resistivity ρ_{∞} on Co content is studied.

REFERENCES

1. A. Vassiliev, *J. Magn. Magn. Mater.* **242-245**, 66 (2002).
2. L.I. Kosse, V.V. Zaitsev, V.G. Munenin, V.S. Kartashov, E.D. Politova, M.A. Sevost'yanov, *FMM* **2**, 48 (1992).
3. M. Senda, Y. Nagai, *J. Appl. Phys.* **65** No8, 3157 (1989).
4. M. Volmer, J. Neamtu, *J. Magn. Magn. Mater.* **316**, e265 (2007).
5. H. Maeda, *J. Appl. Phys.* **53** No5, 3735 (1982).
6. *Tekhnologiya tonkih plenok: Spravochnik (Red. L. Maissel, R. Glang)* (M.: Sov. radio: 1977).
7. I.Yu. Protsenko, *Tekhnologiya ta fizyka tonkyh metalevyh plivok* (Sumy: Vyd-vo SumDU: 2000).
8. S.S. Gorelik, Yu.A. Skakov, L.N. Rastorguev, *Rentgenograficheskiy i elektronno-opticheskiy analiz: Prilozheniya* (M.: Metallurgiya: 1971).
9. *Diagrammy sostoyaniya dvoynyh metallicheskih sistem (Red. N.P. Lyakishev)* (M.: Mashinostroenie: 1996).
10. V.G. Pushin, S.G. Blinov, L.I. Yurchenko, *FMM* **75** No3, 96 (1993).
11. A.I. Kuz'menko, T.A. Prokof'eva, I.E. Protsenko, V.G. Shamonya, L.A. Yaremenko, *Izv. AN SSSR, Ser.fiz.* **8**, 1590 (1986).
12. S.V. Sukhvalo, *Struktura i magnitnye svoistva magnitnyh plenok zhelezo-nikel'-kobal'tovyh splavov* (Minsk: Nauka i tekhnika: 1974).
13. I.E. Protsehko, M.D. Smolin, A.V. Yaremenko, V.B. Loboda, *UFZh* **33** No6, 875 (1988).
14. O.V. Sadyreva, Yu.E. Lapshova, I.G. Korshunov, S.G. Taluts, V.F. Polev, V.I. Gorbatov, *Phys. Met. Metallogr.* **89** No2, 206 (2000).